

Light propagation in nanorod arrays

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We study propagation of TM- and TE-polarized light in two-dimensional arrays of silver nanorods of various diameters in a gelatin background. We calculate the transmittance, reflectance and absorption of arranged and disordered nanorod arrays and compare the exact numerical results with the predictions of the Maxwell-Garnett effective-medium theory. We show that interactions between nanorods, multipole contributions and formations of photonic gaps affect strongly the transmittance spectra that cannot be accounted for in terms of the conventional effective-medium theory. We also demonstrate and explain the degradation of the transmittance in arrays with randomly located rods as well as weak influence of their fluctuating diameter. For TM modes we outline the importance of skin-effect, which causes the full reflection of the incoming light. We then illustrate the possibility of using periodic arrays of nanorods as high-quality polarizers.

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I. INTRODUCTION

Resonance properties of nanoparticles have been observed for centuries thanks to beautiful colors of gold- and silver-patterned stained glasses. Over the last decade nanopatterned materials have attracted even increased attention due to their unique electronic and optical characteristics. Nowadays, they are considered as promising candidates for wide variety of applications in sub-wavelength waveguiding^{1,2}, enhanced Raman scattering spectroscopy³, non-linear optics⁴, photovoltaics⁵ and biological/medical sensing⁶ and many others.

A characteristic size of metallic nanoparticles d is about an order of magnitude smaller than the wavelength of incoming light λ , which can excite collective oscillations of electron density inside the particle, - plasmons. The plasmon excitation results in an enhanced extinction (extinction = absorption + scattering) as well as an increased intensity of the electromagnetic field near the particle⁷.

The important issue that makes nanoparticles so attractive for sensing applications is the effect of the geometry and size of nanoparticles and surrounding environment on a position of the plasmonic resonance^{7,8,9,10}. For example, the presence of antibodies in cells affected by cancer modifies the environment for the gold nanoparticles placed on a tissue and results in a shift of extinction peak that can be easily imaged by conventional microscopy¹¹.

Recently it has also been demonstrated^{12,13} that embedding metallic nanoparticles into a polymeric matrix provides the larger contrast in the effective refractive index of the blend material, being much lower or higher than that of a pure polymer. Developing such the materials can facilitate creating high-contrast-index photonic polymer crystals.

Nanoparticles assembled in nanochains can also be applied as subwavelength waveguides^{2,15}. In the case of closely placed particles the coupling (and light propaga-

tion) arises from the evanescent dipole field from each particle, which excites a plasmon on its neighbour. This excitation travels along the chain, making the electron density within all the particles oscillate in resonance.

In the present paper we will focus on light propagation in large arrays of infinitely long nanorods. Prototypes of such the arrays have been recently fabricated experimentally^{16,17}. These arrays represent randomly oriented or aligned long rods (or spikes) of a material (dielectric or metal), several tens of nanometers in diameter. Despite of significant progress in nanofabrication technologies, to our knowledge, however, the theoretical description of light propagation in nanorod arrays is still missing.

The paper is organized as follows. In Section II we outline transmittance properties of nanorod arrays within the framework of the Maxwell-Garnett effective-medium theory. In Section III we present numerical modeling of light propagation through periodic arrays of nanorods and compare the results with the predictions of the Maxwell-Garnett theory. In Section IV the effect of various types of disorder is studied.

II. EFFECTIVE MEDIUM THEORY

We consider a gelatin matrix with an embedded two-dimensional array of silver nanorods. The effective dielectric function $\varepsilon_{eff}(\omega)$ of that composite can be estimated from developed for more than 100 years ago Maxwell-Garnett theory⁷:

$$\frac{\varepsilon_{eff}(\omega) - \varepsilon_{mat}}{\varepsilon_{eff}(\omega) + 2\varepsilon_{mat}} = f \frac{\varepsilon_{rod}(\omega) - \varepsilon_{mat}}{\varepsilon_{rod}(\omega) + 2\varepsilon_{mat}}, \quad (1)$$

where $f = S_2/S_1$ is the filling factor of the nanorods embedded into the matrix, S_1 is the active area of the matrix and S_2 is the total cross-section area of the

nanorods. The dielectric function of the gelatin matrix is $\varepsilon_{mat} = 2.25$. The dielectric function $\varepsilon_{rod}(\omega)$ of the nanorods is taken from the SOPRA database¹⁸ for the bulk material. The Maxwell-Garnet theory is valid for relatively small nanoparticles (nanorods) (up to several tens of nanometers) at low concentrations (less than 30%). The dielectric function (here and hereafter all the spectra are given in respect of light wavelength in vacuum λ_0) of the Ag(10%)-gelatin blend is presented in Fig. 1 (a).

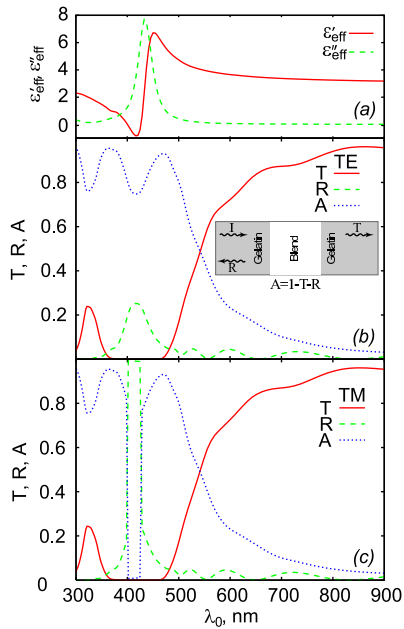


FIG. 1: (Color online) (a) Dielectric function of a blend of silver nanorods (nanoparticles) with the concentration 10% embedded into a gelatin background. Transmittance, reflectance and absorption of the TE (b) and TM (c) modes propagating through a $0.7\mu\text{m}$ thick layer of Ag(10%)-gelatin blend. Inset in (b) outlines the system under study.

The dielectric function in Fig. 1 (a) characterizes the blend as a highly-dispersive lossy material with an absorption peak centered around 414 nm. According to the Mie's theory this peak corresponds the plasmon resonance of a single Ag spherical nanoparticle in gelatin, the position of the peak obeys the well-known relation $\varepsilon_{rod} = -2\varepsilon_{mat}$ ⁷. In order to study light propagation through the layer of the blend we consider a 2D “sandwich-like” structure consisting of semi-infinite gelatin “waveguides” connected to the blend region [see inset to Fig. 1 (b)]. The structure is assumed to be infinite in z -direction, thus the solution to the Maxwell's equations decouples into TE (vector of a magnetic field is parallel to z) and TM (vector of an electric field is parallel to z). The transmission, reflection and absorption for both polarizations are given in Fig. 1 (b) and (c) respectively.

It is easy to see that for both TE and TM polarizations there exists a gap (or a stop-band) in the transmission caused by the enhanced absorption near the extinction

resonance peak. However, the reflectance and absorption within the stop-band possess distinct behavior for different polarizations. When the real part of the dielectric constant of the blend becomes negative ($400 < \lambda_0 < 425$ nm) the reflectance of the TE mode increases due to increased contrast against the dielectric function of the gelatin matrix (which causes a dip in the absorption). At the same time, for TM-polarized light the reflectance sharply increases up to 1 because of the metallic character of the blend in this region and enhanced skin effect. For both polarizations Bragg's reflections from the boundaries of the blend region, manifested themselves as minima and maxima, are clearly seen for $\lambda_0 > 500$ nm.

Despite its adequacy for small isolated circular nanoparticles, a simple Maxwell-Garnet theory, however, has certain limitations. Namely, it does not account for the shape and distribution of metal clusters in the dielectric medium, neglecting important polarization properties of both single non-circular particles and their arrangements^{19,20}. In order to incorporate these features and study transmission characteristics of periodic and disordered nanorod arrays we apply the recursive Green's function technique²¹.

III. PERIODIC NANOROD ARRAYS

We now focus on 2D arrays of infinitely long silver nanorods arranged as a square lattice in a gelatin background. Keeping the filling factor of Ag, $f = 10\%$, constant, we consider two cases, (a) a finite-size lattice with thickness $a = 0.7\mu\text{m}$ of nanorods with the diameter $d = 10\text{nm}$, and (b) the lattice of the same width assembled from nanorods of 60 nm in diameter, see Fig. 2. Lattice constants are 29 and 175 nm for cases (a) and (b) respectively.

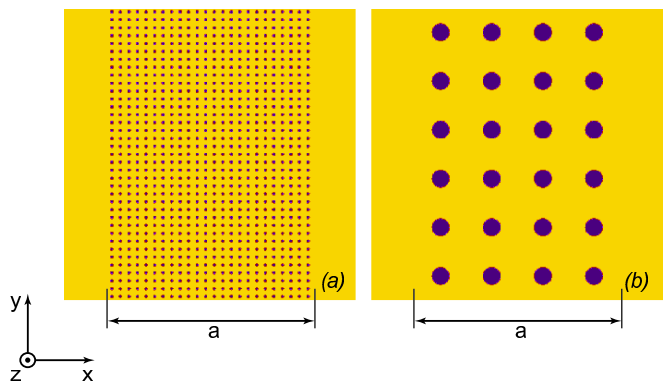


FIG. 2: (Color online) Arrays of silver nanorods with diameter (a) 10 nm, and (b) 60 nm embedded in an infinite gelatin background. For both cases the thickness of the layer $a = 0.7\mu\text{m}$ and the filling factor $f=10\%$.

Such the choice of nanorod sizes is motivated by the essential difference in polarization properties of small and

large nanoparticles¹⁰. If the nanoparticle is small enough ($d \ll \lambda_0$), according to the Mie's theory, only the dipole plasmonic oscillations contribute to the extinction spectra, whereas for larger particles higher-order resonances contribute to the spectra as well¹⁰. Using the recursive Green's function technique we perform numerical simulations for both TE and TM polarizations of light falling normally from the left to the boundary between gelatin and the blend.

A. TE-modes

When a nanosized metallic nanoparticle is illuminated by light, the electric components of an electromagnetic field excite collective oscillations of electronic plasma inside the particles – plasmons. If the particles are arranged into chains, these plasmonic oscillations possess a resonant character that facilitates the propagation of light along the chain. Such the chains have been intensively studied in literature² as promising candidates for sub-wavelength wave-guiding.

Let us irradiate the array of infinitely long nanorods with TE-polarized light. In this case E_x and E_y components of the electromagnetic field excite coherent plasmonic oscillations on each nanorod. Figure 3 shows the calculated transmittance, reflectance and absorption of a TE mode propagating through the arrays of nanorods.

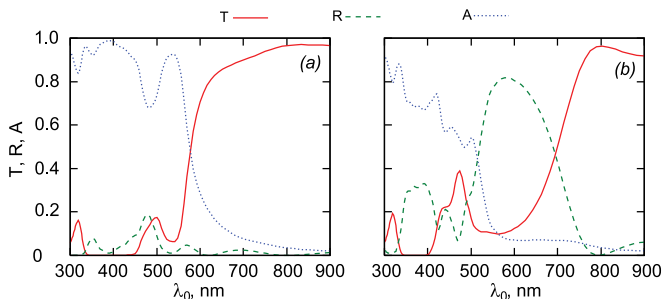


FIG. 3: (Color online) Transmittance, reflectance and absorption of a TE mode travelling through the square arrays of nanorods with diameter (a) 10 nm and (b) 60 nm (see Fig. 2 for details).

Small nanorods. Let us first concentrate on an array of nanorods with the diameter 10 nm [Fig. 3 (a)]. In the spectra one can clearly distinguish two regions, namely the region of high absorption ($\lambda_0 < 600$ nm), containing a wide main absorption peak at 414 nm, two minor peaks at 350 and 530 nm and the region of high transmittance ($\lambda_0 > 600$ nm). Now we will take a closer look at these regions separately.

The position of the main extinction resonance agrees well with that obtained from Eq. (1). However, in contrast to the Maxwell-Garnett theory, the spectrum contains two minor peaks near 350 and 530 nm. In order to explain them one needs to account the effect of coupling

between several nanorods. For this sake we compare light propagation through (a) a single isolated nanorod (diameter 10 nm), (b) two coupled nanorods aligned parallel to the light propagation direction, (c) those aligned perpendicularly, and (d) four coupled nanorods. These four cases are presented in Fig. 4.

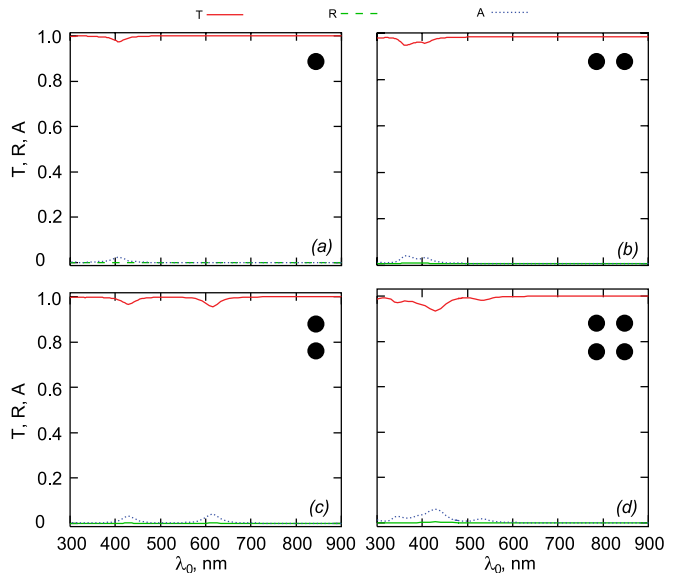


FIG. 4: (Color online) Transmittance, reflectance and absorption of a single (a), a pair of horizontally (b) and vertically (c) aligned, and (d) four coupled nanorods for the TE-polarized light. The inter-rod distances are taken 29 nm, equal the lattice constant for the array (Fig. 2 (a)). The size of the computational domain is also the same as that for the nanorod arrays in Fig. 2.

For the case of a single isolated rod [Fig. 4 (a)] only one peak near 410 nm emerges which is in a good agreement with the analytical value of 414 nm. For the cases (b) and (c) of twin coupled nanorods the additional peaks, centered at 355 and 620 nm respectively, appear. Their origin has been thoroughly studied in¹⁹ and clarified in terms of enhanced [case (b)] and weakened [case (c)] restoring forces between the particles. However, for the system of four particles (d) these forces partially compensate each other, and the minor resonances move closer towards the main peak.

Let us now focus on the wavelength region $\lambda_0 > 600$ nm, where TE-polarized light propagates at high transmittance. In order to understand this behavior, we complement the transmission coefficient with the band diagram of the nanorod array. It should be mentioned that, in general, a band diagram represents propagating Bloch states (states with real eigenvalues). However, as the metallic rods (or nanoparticles) are absorbing, all the states in the blend will be decaying and eventually die off at the infinity. Yet all the Bloch eigenvalues in such systems have imaginary components. In Fig. 5 (a) we represent a band structure (real parts of eigenvalues) in

Γ X-direction for the states with the smallest imaginary parts.

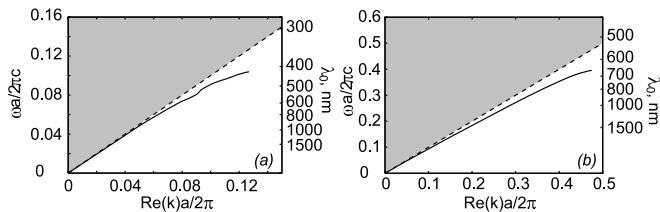


FIG. 5: Band diagrams of the nanorod arrays from Fig. 2 (a) and (b) respectively. The dashed line outlines the light cone.

The dispersion curve in Fig. 5 (a) has a small bump around 550 nm, which is caused by the minor extinction resonance. The band is located very close to the light line that results in a rather strong coupling between the incoming light and the plasmonic Bloch states of the blend region. Such the strong coupling explains high transmittance in the red wavelength region.

Large nanorods For nanorods with the diameter 60 nm, the position of the main extinction peak agrees with that one of the small particles. However, there is an essential difference in physics behind. When the diameter of a nanoparticle increases, higher-order dipole oscillations now contribute the resulting extinction spectrum⁷. It has been recently shown¹⁰ that the peak centered at ≈ 400 nm is due to the *quadruple* resonance of a nanorod, whereas the dipole resonance is redshifted and overlaps with the region of the enhanced reflectance ($500 < \lambda_0 < 700$ nm). The indication in favor of this interpretation is a narrower width of the stop-band in the transmission (60 nm against 100 nm in case of small rods). This is because the higher-order dipole interactions causing the stop-band behaviour for the case of large nanorods are generally weaker.

Now let us clarify the origin of the high-reflectance region. The lattice constant for this structure is 175 nm. This is of the same order as the wavelength of light, such that the structure effectively represents a two-dimensional photonic crystal. The plasmonic band in Fig. 5 (b) extends from $\omega a/2\pi c = 0$ to 0.4 ($\lambda_0 \approx 660$ nm) where it experiences a *photonic bandgap* that causes the high reflectance of the structure. This bandgap overlaps with the tail of the extinction peak near 500 nm (see Fig. 3).

B. TM-modes

Let us now consider the TM-polarization of the incoming light. Figure 6 (a) shows the transmittance, reflectance and absorption of the TM-polarized light for the small nanorods. In contrast to the Maxwell-Garnett picture (Fig. 1), almost for the whole wavelength range under study light does not penetrate the region occupied by nanorods and gets fully reflected back, resulting in

zero transmittance. This discrepancy can be explained by the skin-effect on the silver rods. At the same time, the Maxwell-Garnett theory (1) fully disregards the important screening properties of the rods, simply averaging the effective dielectric constant over the structure. It is also worth mentioning, that as we consider infinitely long nanorods, incoming TM-mode *does not excite* any plasmons on the rods and thus there is no plasmonic contribution in overall transmission.

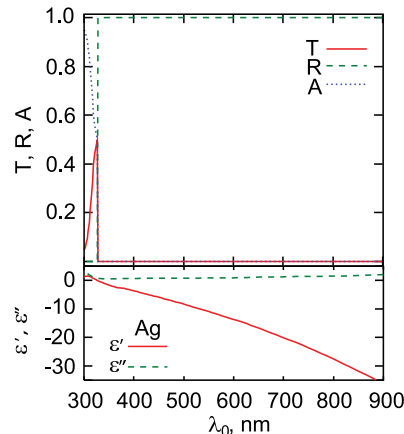


FIG. 6: (Color online) (a) Transmission, reflection and absorption coefficients of the TM-mode through a nanorod array of $d = 10$ nm. Due to the skin-effect light does not penetrate the blend region. For $\lambda_0 < 328$ nm the real part ϵ' of the dielectric function of silver (b) becomes positive and the transmission coefficient abruptly increases.

However, for very short wavelengths ($\lambda_0 \lesssim 328$ nm) the real part of the dielectric function of silver becomes positive (see Fig. 6 (b)) and the blend behaves like a lossy dielectric rather than a metal. This results in non-zero transmission in this region.

The obtained results clearly show that resonant plasmonic oscillations in periodic nanorod arrays represent a dominating light propagation mechanism for the TE-polarized light, whereas for the TM modes the nanorod structure represents practically a perfect screen. This features can be utilized in a nearly 100% effective polarizer.

IV. DISORDERED NANOROD ARRAYS

As we have demonstrated in the preceding section, TE-polarized incident light in off-resonance wavelength region propagates through periodic arrays of small nanorods at very high transmission. Now we introduce some disorder in this array and consider two separate cases, namely when nanorods are arranged in a square lattice but have randomly varying diameter, and rods of equal diameter, randomly distributed within the layer. For both cases the filling factor $f = 10\%$ is kept constant, the distribution is taken uniform. Figures 7 (a, c) and

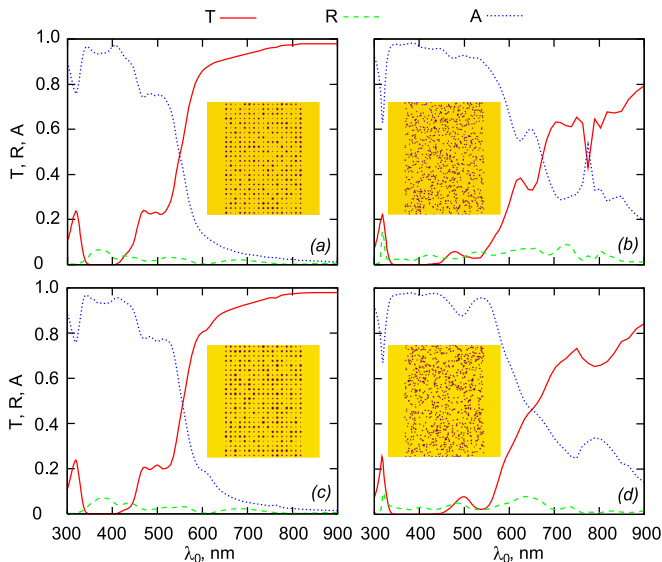


FIG. 7: (Color online) Transmission, reflection and absorption coefficients of the TE-polarized light propagating through disordered nanorod arrays. (a, c) Two different configurations of nanorods arranged in a square lattice, their d diameter randomly varies from 5 to 20 nm. (b, d) Nanorods with fixed $d = 10$ nm are randomly distributed within the layer. Insets show the actual geometries of the structures.

(b, d) demonstrate the transmittance, reflectance and absorption for both cases.

The transmission characteristics for the structure with the random diameter of nanorods [Fig. 7 (a, c)] closely resemble those for the array of fixed-sized nanoparticles [Fig. 3 (a)]. The main difference is that weaker dipole interactions between adjacent particles of different diameter cause a minor narrowing of the stop-band (60 nm versus 100 nm in the ideal case) and a slight degradation of the minor extinction peak. It should be emphasized that the transmission properties of arrays with different distributions of the nanorod diameter [Fig. 7 (a) and (c)] are virtually the same.

For the case of the randomly distributed equal-sized nanorods [Fig. 7 (b, d)] the situation changes. In contrast to the previous case of the ordered nanorod array with random diameter, the absorption spectra in the region $\lambda_0 > 600$ nm are extremely sensitive to the geometry of the structure. It is interesting to note how clustering of nanorods manifests itself. The overall absorption in the region $\lambda_0 > 600$ nm is much higher (and the transmission is lower) in comparison to the periodic lattice, as it consists of the averaged multiple absorption peaks of closely situated, touching or overlapping nanorods. Since the inter-rod distances are not constant any longer, each single rod is now affected by many dipole interactions of different strengths from neighboring rods. Reflectances, however, are practically identical and not significantly higher than for the periodic case. It can be explained that due to its non-periodicity this structure absorbs bet-

ter than reflects. The clustering and more complex interactions of nanorods influence the region $\lambda_0 < 600$ nm as well. The main and minor absorption peaks for the structure Fig. 7 (b) almost overlap, whereas for Fig. 7 (d) are still well-separated.

We should specially mention that in order to incorporate the effect of nanoparticle aggregates into Maxwell-Garnett theory, several approaches were suggested⁷ (see also references therein). In that case the effective medium dielectric function is derived by inserting the total aggregate polarizabilities instead of that of a single isolated particle into the Maxwell-Garnett theory.

V. CONCLUSIONS

We have studied propagation of TE- and TM-polarized light in two-dimensional arrays of silver nanorods in a gelatin background. In order to calculate transmittance, reflectance and absorption in arrays of ordered and disordered nanorods we applied the recursive Green's function technique and compared the obtained numerical results with predictions of the Maxwell-Garnett effective-medium theory. We have demonstrated that this theory describes adequately only the case of the TE-polarized light propagating in ordered arrays of small (~ 10 nm), well-separated nanorods and only in the frequency interval outside the main plasmonic resonance.

Our numerical calculations outline the importance of geometrical factors such as the size of the rods and their distribution. In particular, we have demonstrated, that interaction between adjacent nanorods brings the significant contribution to the transmission spectra, which is manifested as additional absorption peaks (that are missing in the effective-medium approach). The Maxwell-Garnett theory also disregards both the impacts of higher-order dipole contributions and formation of photonic band gaps in the case of arrays of large nanorods.

We have also studied the effect of disorder on the transmittance of the nanorod arrays. We have introduced two types of disorder, (a) ordered array with randomly varying nanorod diameters, and (b) a random distribution of nanorods of the same size within the blend. The disorder in rod placement leads to a strong suppression of the transmission (and the enhanced absorption) due to plasmonic resonances related to the clustering of the rods. We have demonstrated that clustering effects are sensitive to the actual geometry of the structure. In contrast, the impact of randomly varying diameters of the rods is much less profound.

Despite its partial adequacy for the TE-polarized light, the Maxwell-Garnett effective-medium theory is shown to be invalid for the case of TM polarization. It simply averages the effective dielectric function inside the blend, missing the important screening properties of the metallic nanorods and characterizing the blend as a (partially) transparent medium. In contrast, the numerical modelling shows the strong skin effect that fully prohibits the

propagation of the TM modes through the structure. The region of high transmittance for the TE modes and the strong skin effect for the TM modes makes the nanorod arrays promising candidates for high-quality polarizers.

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